MICROWAVE SPECTRUM OF A SUPERACID AND ITS MONOHYDRATE: TUNNELING AND LARGE AMPLITUDE MOTION IN CF_3SO_2OH AND CF_3SO_2OH-H_2O

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The triflic acid monomer (CF_3SO_2OH) and its 1:1 complex with water (CF_3SO_2OH-H_2O) have been observed by chirped-pulse and cavity Fourier transform microwave spectroscopy. A pair of tunneling states was identified in the rotational spectra for both species. For CF_3SO_2OH, the assignment of *b*-type spectra led to the direct measurement and experimental determination of the tunneling energy (ΔE = 52.96704(90) MHz). M06-2X/6-311++G(3df,3pd) calculations predict a 2.8 kcal/mol barrier for the tunneling motion of the hydroxyl proton rotating around the S-O bond through a transition state in which the O-H is oriented *anti* with respect to the CF_3 group. A complete 360° scan of the hydroxyl proton around the S-O bond shows an additional transition state in the *syn* orientation resulting in a 6.2 kcal/mol barrier. In the CF_3SO_2OH-H_2O complex, spectral doublets were observed with an approximate 3:1 intensity ratio indicative of an equivalent exchange of the protons in H_2O resulting from rotation about its C_2 axis. The proposed water motion is further supported by the quenching of the spectral pairs for the asymmetrically deuterated CF_3SO_2OH-DOH complex. Despite the strong acidity of triflic acid, no evidence of protonation of the water was observed.